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TRANSMITTAL LETTER TO THE UNITED STATES

ATTORNEY'S DOCKET NUMBER 50512

DESIGNATED/ELECTED OFFICE (DO/EO/US)  
CONCERNING A FILING UNDER 35 U.S.C. 371

U.S. APPLICATION NO. (If known, see 37 CFR 1.5)

INTERNATIONAL APPLICATION NO.	INTERNATIONAL FILING DATE	PRIORITY DATE CLAIMED
PCT/EP00/07003	21 July 2000	23 July 1999

TITLE OF INVENTION: PREPARATION OF GLYPHOSATE OR A SALT THEREOF

APPLICANT(S) FOR DO/EO/US Ulrich MUELLER, Hans Rupert MERKLE

Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:

1. /X/ This is a FIRST submission of items concerning a filing under 35 U.S.C. 371.
2. / / This is a SECOND or SUBSEQUENT submission of items concerning a filing under 35 U.S.C. 371.
3. /X/ This express request to begin national examination procedures (35 U.S.C. 371(f)) at any time rather than delay examination until the expiration of the applicable time limit set in 35 U.S.C. 371(b) and PCT Articles 22 and 39(1).
4. /x/ A proper Demand for International Preliminary Examination was made by the 19th month from the earliest claimed priority date.
5. /X/ A copy of the International Application as filed (35 U.S.C. 371(c)(2)).
  - a. /X/ is transmitted herewith (required only if not transmitted by the International Bureau).
  - b. / / has been transmitted by the International Bureau.
  - c. / / is not required, as the application was filed in the United States Receiving Office (RO/USO).
6. /X/ A translation of the International Application into English (35 U.S.C. 371(c)(2)).
7. / / Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371(c)(3)).
  - a. / / are transmitted herewith (required only if not transmitted by the International Bureau).
  - b. / / have been transmitted by the International Bureau.
  - c. / / have not been made; however, the time limit for making such amendments has NOT expired.
  - d. / / have not been made and will not be made.
8. / / A translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)).
9. /X/ An oath or declaration of the inventor(s) (35 U.S.C. 371(c)(4)).
10. / / A translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371(c)(5)).

Items 11. to 16. below concern other document(s) or information included:

11. / / An Information Disclosure Statement under 37 CFR 1.97 and 1.98.
12. /X/ An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.
13. /x/ A FIRST preliminary amendment.  
/ / A SECOND or SUBSEQUENT preliminary amendment.
14. / / A substitute specification.
15. / / A change of power of attorney and/or address letter.
16. /x/ Other items or information.  
International Search Report  
International Preliminary Examination Report

U.S. Appln. No. (If Known) INTERNATIONAL APPLN. NO.  
PCT/EP00/ 07003

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	CALCULATIONS	PTO USE ONLY
17. /X/ The following fees are submitted BASIC NATIONAL FEE (37 CFR 1.492(a)(1)-(5)): Search Report has been prepared by the EPO or JPO.....\$890.00	890.00	
International preliminary examination fee paid to USPTO (37 CFR 1.482).....\$710.00		
No international preliminary examination fee paid to USPTO (37 CFR 1.482) but international search fee paid to USPTO (37 CFR 1.445(a)(2)).....\$740.00		
Neither international preliminary examination fee (37 CFR 1.482) nor international search fee (37 CFR 1.445(a)(2)) paid to USPTO .....\$ 1,040.00		
International preliminary examination fee paid to USPTO (37 CFR 1.482) and all claims satisfied pro -visions of PCT Article 33(2)-(4).....\$100.00		
<b>ENTER APPROPRIATE BASIC FEE AMOUNT = \$ 890.00</b>		
Surcharge of \$130.00 for furnishing the oath or declaration later than / / 20 / / 30 months from the earliest claimed priority date (37 CFR 1.492(e)).		
<u>Claims</u>	<u>Number Filed</u>	<u>Number Extra</u>
Total Claims	18 -20	X\$18.
Indep. Claims	1 -3	X\$84.
Multiple dependent claim(s) (if applicable)		+280.
<b>TOTAL OF ABOVE CALCULATION</b>		<b>= 890.</b>
Reduction of 1/2 for filing by small entity, if applicable. Verified Small Entity statement must also be filed (Note 37 CFR 1.9, 1.27, 1.28).		
<b>SUBTOTAL</b>		<b>= 890.</b>
Processing fee of \$130. for furnishing the English translation later than / / 20 / / 30 months from the earliest claimed priority date (37 CFR 1.492(f)).		
<b>TOTAL NATIONAL FEE</b>		<b>= 890.</b>
Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31) \$40.00 per property		
<b>TOTAL FEES ENCLOSED</b>		<b>= \$ 930.00</b>
		Amount to be refunded: \$ Charged \$

a./X/ A check in the amount of \$ 930.00 to cover the above fees is enclosed.

b./ / Please charge my Deposit Account No. \_\_\_\_\_ in the amount of \$ \_\_\_\_\_ to cover the above fees. A duplicate copy of this sheet is enclosed.

c./X/ The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any overpayment to Deposit Account No. 11-0345. A duplicate copy of this sheet is enclosed.

**NOTE:** Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137(a) or (b) must be filed and granted to restore the application to pending status.

**SEND ALL CORRESPONDENCE TO:**  
KEIL & WEINKAUF  
1101 Connecticut Ave., N.W.  
Washington, D. C. 20036

  
SIGNATURE

Herbert B. Keil  
NAME  
Registration No. 18,967

10/031234  
531 Rec'd PCT/PT. 17 JAN 2002

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re the Application of )  
MUELLER et al. ) BOX PCT  
)  
International Application )  
PCT/EP 00/07003 )  
)  
Filed: July 21, 2000 )  
)

For: PREPARATION OF GLYPHOSATE OR A SALT THEREOF

PRELIMINARY AMENDMENT

Honorable Commissioner of  
Patents and Trademarks  
Washington, D.C. 20231

Sir:

Prior to examination, kindly amend the above-identified application as follows:

IN THE CLAIMS

Kindly cancel claim 1-6 and insert new claims 7-24 as shown on the attached sheets.

R E M A R K S

New claims 7-24 have replaced claims 1-6 and to place the claims in better form for  
U.S. filing. No new matter is included.

A clean copy of the claims is attached.

Favorable action is solicited.

Respectfully submitted,

KEIL & WEINKAUF

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(202)659-0100

10031234-011702

**NEW CLAIMS 7-24 - OZ 0050/50512**

- 10031234-04702
- 7. A process for preparing N-phosphonomethylglycine or a salt thereof by bringing phosphonomethyliminodiacetic acid or a salt thereof into contact with at least one oxygen-containing oxidant in the presence of a heterogeneous catalyst comprising at least one silicate.
8. A process as claimed in claim 7, wherein the oxygen-containing oxidant or oxidants is/are selected from the group consisting of hydroperoxides, gases containing molecular oxygen, oxygen-donating compounds, nitrogen oxides and mixtures of two or more thereof.
9. A process as claimed in claim 7, wherein the silicate or silicates is/are selected from the group consisting of zeolites, sheet silicates, naturally occurring or synthetically produced clay minerals, clathrasils and mixtures of two or more thereof.
10. A process as claimed in claim 8, wherein the silicate or silicates is/are selected from the group consisting of zeolites, sheet silicates, naturally occurring or synthetically produced clay minerals, clathrasils and mixtures of two or more thereof.
11. A process as claimed in claim 7, wherein the crystalline silicate or silicates is/are selected from the group consisting of zeolites of the structure types ABW, ACO, AEI, AEL, AEN, AET, AFG, AFI, AFN, AFO, AFR, AFS, AFT, AFX, AFY, AHT, ANA, APC, APD, AST, ATN, ATO, ATS, ATT, ATV, AWO, AWW, BEA, BIK, BOG, BPH, BRE, CAN, CAS, CFI, CGF, CGS, CHA, CHI, CLO, CON, CZP,

**NEW CLAIMS 7-24 - OZ 0050/50512**

DAC, DDR, DFO, DFT, DOH, DON, EAB, EDI, EMT, EPI, ERI, ESV, EUO, FAU, FER, GIS, GME, GOO, HEU, IFR, ISV, ITE, JBW, KFI, LAU, LEV, LIO, LOS, LOV, LTA, LTL, LTN, MAZ, MCM-22, MEI, MEL, MEP, MER, MFI, MFS, MON, MOR, MSO, MTF, MTN, MTT, MTW, MWW, NAT, NES, NON, OFF, OSI, PAR, PAU, PHI, RHO, RON, RSN, RTE, RTH, RUT, SAO, SAT, SBE, SBS, SBT, SFF, SGT, SOD, STF, STI, STT, TER, THO, TON, TSC, VET, VFI, VNI, VSV, WEI, WEN, YUG, ZON and ITQ-4 and mixtures of two or more thereof.

12. A process as claimed in claim 8, wherein the crystalline silicate or silicates is/are selected from the group consisting of zeolites of the structure types ABW, ACO, AEI, AEL, AEN, AET, AFG, AFI, AFN, AFO, AFR, AFS, AFT, AFX, AFY, AHT, ANA, APC, APD, AST, ATN, ATO, ATS, ATT, ATV, AWO, AWW, BEA, BIK, BOG, BPH, BRE, CAN, CAS, CFI, CGF, CGS, CHA, CHI, CLO, CON, CZP, DAC, DDR, DFO, DFT, DOH, DON, EAB, EDI, EMT, EPI, ERI, ESV, EUO, FAU, FER, GIS, GME, GOO, HEU, IFR, ISV, ITE, JBW, KFI, LAU, LEV, LIO, LOS, LOV, LTA, LTL, LTN, MAZ, MCM-22, MEI, MEL, MEP, MER, MFI, MFS, MON, MOR, MSO, MTF, MTN, MTT, MTW, MWW, NAT, NES, NON, OFF, OSI, PAR, PAU, PHI, RHO, RON, RSN, RTE, RTH, RUT, SAO, SAT, SBE, SBS, SBT, SFF, SGT, SOD, STF, STI, STT, TER, THO, TON, TSC, VET, VFI, VNI, VSV, WEI, WEN, YUG, ZON and ITQ-4 and mixtures of two or more thereof.

**NEW CLAIMS 7-24 - OZ 0050/50512**

13. A process as claimed in claim 9, wherein the crystalline silicate or silicates is/are selected from the group consisting of zeolites of the structure types ABW, ACO, AEI, AEL, AEN, AET, AFG, AFI, AFN, AFO, AFR, AFS, AFT, AFX, AFY, AHT, ANA, APC, APD, AST, ATN, ATO, ATS, ATT, ATV, AWO, AWW, BEA, BIK, BOG, BPH, BRE, CAN, CAS, CFI, CGF, CGS, CHA, CHI, CLO, CON, CZP, DAC, DDR, DFO, DFT, DOH, DON, EAB, EDI, EMT, EPI, ERI, ESV, EUO, FAU, FER, GIS, GME, GOO, HEU, IFR, ISV, ITE, JBW, KFI, LAU, LEV, LIO, LOS, LOV, LTA, LTL, LTN, MAZ, MCM-22, MEI, MEL, MEP, MER, MFI, MFS, MON, MOR, MSO, MTF, MTN, MTT, MTW, MWW, NAT, NEW, NON, OFF, OSI, PAR, PAU, PHI, RHO, RON, RSN, RTE, RTH, RUT, SAO, SAT, SBE, SBS, SBT, SFF, SGT, SOD, STF, STI, STT, TER, THO, TON, TSC, VET, VFI, VNI, VSV, WEI, WEN, YUG, ZON and ITQ-4 and mixtures of two or more thereof.
14. A process as claimed in claim 10, wherein the crystalline or silicates is/are selected from the group consisting of zeolites of the structure types ABW, ACO, AEI, AEL, AEN, AET, AFG, AFI, AFN, AFO, AFR, AFS, AFT, AFX, AFY, AHT, ANA, APC, APD, AST, ATN, ATO, ATS, ATT, ATV, AWO, AWW, BEA, BIK, BOG, BPH, BRE, CAN, CAS, CFI, CGF, CGS, CHA, CHI, CLO, CON, CZP, DAC, DDR, DFO, DFT, DOH, DON, EAB, EDI, EMT, EPI, ERI, ESV, EUO, FAU, FER, GIS, GME, GOO, HEU, IFR, ISV, ITE, JBW, KFI, LAU, LEV, LIO, LOS,

**NEW CLAIMS 7-24 - OZ 0050/50512**

LOV, LTA, LTL, LTN, MAZ, MCM-22, MEI, MEL, MEP, MER, MFI, MFS, MON, MOR, MSO, MTF, MTN, MTT, MTW, MWW, NAT, NES, NON, OFF, OSI, PAR, PAU, PHI, RHO, RON, RSN, RTE, RTH, RUT, SAO, SAT, SBE, SBS, SBT, SFF, SGT, SOD, STF, STI, STT, TER, THO, TON, TSC, VET, VFI, VNI, VSV, WEI, WEN, YUG, ZON and ITQ-4 and mixtures of two or more thereof.

15. A process as claimed in claim 7, wherein the at least one heterogeneous catalyst further comprises at least one element selected from among the elements of groups Ia, IIa, IIIa, IVa, Va, VIa, VIIa, VIIIa, Ib, IIb, IIIb, IVb, Vb, VIb, VIIb of the Periodic Table.
16. A process as claimed in claim 8, wherein the at least one heterogeneous catalyst further comprises at least one element selected from among the elements of groups Ia, IIa, IIIa, IVa, Va, VIa, VIIa, VIIIa, Ib, IIb, IIIb, IVb, Vb, VIb, VIIb of the Periodic Table.
17. A process as claimed in claim 9, wherein the at least one heterogeneous catalyst further comprises at least one element selected from the groups selected from among the elements of groups Ia, IIa, IIIa, IVa, Va, VIa, VIIa, VIIIa, Ib, IIb, IIIb, IVb, Vb, VIb, VIIb of the Periodic Table
18. A process as claimed in claim 10, wherein the at least one heterogeneous catalyst further comprises at least one element selected from among the elements of groups Ia, IIa, IIIa, IVa, Va, VIa, VIIa, VIIIa, Ib, IIb, IIIb, IVb, Vb, VIb, VIIb of the Periodic Table.

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19. A process as claimed in claim 11, wherein the at least one heterogeneous catalyst further comprises at least one element selected from among the elements of groups Ia, IIa, IIIa, IVa, Va, VIa, VIIa, VIIIa, Ib, IIb, IIIb, IVb, Vb, VIb, VIIb of the Periodic Table.
20. A process as claimed in claim 7, wherein the heterogeneous catalyst is regenerated after complete or partial loss of activity and the regenerated heterogeneous catalyst is reused for preparing N-phosphonomethylglycine or a salt thereof from phosphonomethyliminodiacetic acid or a salt thereof.
21. A process as claimed in claim 8, wherein the heterogeneous catalyst is regenerated after complete or partial loss of activity and the regenerated heterogeneous catalyst is reused for preparing N-phosphonomethylglycine or a salt thereof from phosphonomethyliminodiacetic acid or a salt thereof.
22. A process as claimed in claim 9, wherein the heterogeneous catalyst is regenerated after complete or partial loss of activity and the regenerated heterogeneous catalyst is reused for preparing N-phosphonomethylglycine or a salt thereof from phosphonomethyliminodiacetic acid or a salt thereof.
23. A process as claimed in claim 10, wherein the heterogeneous catalyst is regenerated after complete or partial loss of activity and the regenerated heterogeneous catalyst is reused for preparing N-phosphonomethylglycine or a salt thereof from phosphonomethyliminodiacetic acid or a salt thereof.
24. A process as claimed in claim 11, wherein the heterogeneous catalyst is



**NEW CLAIMS 7-24 - OZ 0050/50512**

regenerated after complete or partial loss of activity and the regenerated heterogeneous catalyst is reused for preparing N-phosphonomethylglycine or a salt thereof from phosphonomethyliminodiacetic acid or a salt thereof.--

*as originally filed*

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5                                    **Preparation of glyphosate or a salt thereof**

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10        The present invention relates to a novel process for preparing N-phosphono-  
methylglycine (glyphosate) or a salt thereof by bringing phosphonomethyl-  
iminodiacetic acid (PMIDE) into contact with at least one oxygen-containing  
oxidant in the presence of a heterogeneous catalyst comprising silicates.

15        Processes for preparing glyphosate and its salts are known per se. In all these,  
PMIDE or a salt thereof is reacted with an oxidant, e.g. a hydroperoxide- or an  
oxygen-containing gas, in the presence or absence of a catalyst to form glyphosate  
or a salt thereof. Thus, US 3 954 848 describes the abovementioned reaction in the  
absence of a catalyst using oxidants defined therein at from about 70 to 100°C.

20        The reaction in the presence of gases comprising free oxygen using platinum,  
palladium, rhodium, iridium, ruthenium or osmium as metallic catalyst is described  
in US 3 950 402.

25        US 3 969 398 describes such a reaction in the presence of activated carbon.  
US 4 582 650 describes a process for preparing N-phosphonomethylglycine by  
oxidative cleavage of N-phosphonomethyliminodiacetic acid with simultaneous  
oxidation of the formaldehyde formed as by-product in the presence of a catalyst  
system which comprises activated carbon together with a microporous acid-  
30        resistant aluminosilicate having a ratio of Si to Al of at least 2 as support and a  
noble metal as active component. According to this document, the process is  
carried out so that, or the catalyst is prepared so that, the noble metal is located in  
the pores of the support material and can thus not be poisoned by  
N-phosphonomethylamines.

35        The preparation of salts of glyphosate in the presence of platinum on activated  
carbon using an oxygen-containing gas is described in US 4 147 719.

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The Hungarian patent application HU 187 347 describes such a reaction using peroxides in the presence of a catalytic amount of silver, iron, tin, lead, manganese or molybdenum.

- 5 Such a reaction in aqueous suspension is described in EP-A 0 019 445. A process of the type in question using molecular oxygen in the presence of a catalyst selected from among salts and complex salts of manganese, cobalt, iron, nickel, bromine, ruthenium, aluminum, molybdenum, palladium and/or cerium at temperatures in the range from about 25 to 150°C at atmospheric or  
10 subatmospheric pressure is described in EP-B 0 314 662 and the corresponding parallel patents.

- A process for the selective preparation of secondary amines from tertiary amines, or of primary amines from secondary amines, by means of oxygen or an oxygen-  
15 containing gas in the presence of an activated carbon catalyst whose surface is free of oxides is described in EP-B 0 162 035 and its parallel patents. EP-A 0 464 017 and its parallel patents relate to a process for preparing glyphosate by oxidation of PMIDE by means of a peroxide in the presence of a catalytic amount of iron, zinc, aluminum, palladium or copper or water-soluble V, Fe or Cu compounds.

- 20 The use of water-soluble tungsten compounds or a mixture of a water-soluble tungsten compound and a water-soluble molybdenum compound in a process of the type in question is described in EP-A 0 464 018.

- 25 A process for preparing glyphosate by oxidation of PMIDE under superatmospheric pressure using oxygen or an oxygen-containing gas in the presence of a catalyst comprising noble metal on activated carbon as support is described in EP-B 0 472 693. In this process, the concentration of the noble metal in the reaction medium is reduced to less than 1 ppm.

- 30 A process of the type in question using hydrogen peroxide or oxygen-enriched air at pressures of from 100 to 1 000 bar is described in WO 96/19485.

- The conversion of PMIDE into glyphosate in the presence of H<sub>2</sub>O<sub>2</sub> and activated  
35 carbon is described in WO 96/27602 and in WO 96/38455.

It is an object of the present invention to provide a novel process for preparing

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glyphosate by oxidative treatment of PMIDE, which process gives the target compound glyphosate in high yield.

We have found that this object is achieved by a process for preparing N-phosphonomethylglycine or a salt thereof by bringing phosphonomethyliminodiacetic acid or a salt thereof into contact with at least one oxygen-containing oxidant in the presence of a heterogeneous catalyst comprising at least one silicate.

As indicated above, PMIDE, which can be prepared by methods known from the prior art, is converted into glyphosate in the present process. In addition, salts of PMIDE can be converted into the corresponding glyphosate salts. Suitable salt-forming cations include alkali metals, alkaline earth metals, trimethylsulfonium, guanidinium, urea, ammonium and organic ammonium salts, e.g. the isopropylammonium salt. The latter can be obtained, for example, from organic amines, e.g. alkylamines, alkeneamines and alkanolamines, having not more than two amine groups. Suitable glyphosate salts are described, for example, in US 4 147 719 and WO 96/38455, whose relevant contents are wholly incorporated by reference into the present application. These glyphosate salts are obtained as described below starting from the corresponding PMIDE salts, where the PMIDE salts used as starting materials can likewise be obtained by any methods known from the prior art, e.g. the reaction of PMIDE with, for example, NaOH. According to the present invention, both the monosalts and also the disalts of PMIDE can be used as starting materials and are in turn converted into the corresponding monoglyphosate or diglyphosate salts.

As oxidant in the process of the present invention, it is in principle possible to use any oxygen-containing oxidant. Particular mention may be made of organic peroxides, hydrogen peroxide, oxygen, oxygen-donating compounds and nitrogen oxides, e.g.  $N_2O$ . Organic peroxides include, for example, tert-butyl hydroperoxide, cumene hydroperoxide, peracetic acid, perbenzoic acid, peroxytrifluoroacetic acid, m-chloroperbenzoic acid, benzoyl peroxide, benzenepersulfonic acid. Apart from pure oxygen, all oxygen-containing gases such as air or mixtures of oxygen and inert diluent gases, e.g. helium, argon or nitrogen, can also be used. As oxygen-donating compounds, preference is given to the following:  $H_2O_2$  and  $H_2O_2$  prepared in-situ from  $O_2$  and  $H_2$ . In particular, an aqueous  $H_2O_2$  solution is used; this solution preferably has an  $H_2O_2$  content of from 5 to 60% by weight.

The heterogeneous catalyst used according to the present invention comprises at least one silicate. Here too, it is possible to use all conceivable silicates. In particular, sheet silicates, naturally occurring or synthetically produced clay minerals, zeolites, clathrasils or mixtures of two or more thereof are used as silicates.

Zeolites are, as is known, crystalline aluminosilicates having ordered channel and cage structures and having pore openings in the micropore range below 0.9 nm. The network of such zeolites is built up of  $\text{SiO}_4$  and  $\text{AlO}_4$  tetrahedra which are joined via common oxygen bridges. An overview of the known structures may be found, for example, in M.W. Meier, D.H. Olson, Ch. Baerlocher "Atlas of Zeolite Structure Types", 4th edition, Elsevier, London, 1996.

To balance the negative charge resulting from incorporation of Al(III) into the Si(IV) silicate lattice, exchangeable cations are present in zeolites; in particular, these can be sodium, potassium, lithium or cesium cations, depending on the method of preparation. If these cations are replaced by protons, for example by ion exchange, the corresponding acidic solid having a zeolite structure in the H form is obtained.

Zeolites which contain no aluminum and in whose silicate lattice the Si(IV) is partly replaced by titanium as Ti(IV) are also known. These titanium zeolites, in particular those having a crystal structure of the MFI type, and possible ways of preparing them are described, for example, in EP-A 0 311 983 or EP-A 405 978. Apart from silicon and titanium, such materials can further comprise additional elements such as aluminum, zirconium, tin, iron, cobalt, nickel, gallium, boron or a small amount of fluorine. In the zeolite catalysts used in the process of the present invention, the titanium of the zeolite can be partly or wholly replaced by vanadium, zirconium, chromium or niobium or a mixture of two or more thereof. The molar ratio of titanium and/or vanadium, zirconium, chromium or niobium to the sum of silicon and titanium and/or vanadium and/or zirconium and/or chromium and/or niobium is generally in the range from 0.01:1 to 0.1:1.

It is known that titanium zeolites having an MFI structure can be identified by a particular X-ray diffraction pattern and also by means of a lattice vibration band in the infrared (IR) region at about  $960\text{ cm}^{-1}$ .

Preference is given to using Ti, Ge, Te, V, Cr, Nb, Zr zeolites, in particular Ti zeolites.

5 Specific mention may be made of titanium-, vanadium-, chromium-, niobium- and zirconium-containing zeolites having a pentasil zeolite structure, in particular the types assigned X-ray crystallographically to the ABW, ACO, AEI, AEL, AEN, AET, AFG, AFI, AFN, AFO, AFR, AFS, AFT, AFX, AFY, AHT, ANA, APC, APD, AST, ATN, ATO, ATS, ATT, ATV, AWO, AWW, BEA, BIK, BOG, BPH,  
10 BRE, CAN, CAS, CFI, CGF, CGS, CHA, CHI, CLO, CON, CZP, DAC, DDR, DFO, DFT, DOH, DON, EAB, EDI, EMT, EPI, ERI, ESV, EUO, FAU, FER, GIS, GME, GOO, HEU, IFR, ISV, ITE, JBW, KFI, LAU, LEV, LIO, LOS, LOV, LTA, LTL, LTN, MAZ, MCM-22, MEI, MEL, MEP, MER, MFI, MFS, MON, MOR, MSO, MTF, MTN, MTT, MTW, MWW, NAT, NES, NON, OFF, OSI, PAR,  
15 PAU, PHI, RHO, RON, RSN, RTE, RTH, RUT, SAO, SAT, SBE, SBS, SBT, SFF, SGT, SOD, STF, STI, STT, TER, THO, TON, TSC, VET, VFI, VNI, VSV, WEI, WEN, YUG, ZON and ITQ-4 structures and to mixed structures of two or more of the abovementioned structures. Furthermore, the use of titanium-containing zeolites having the UTD-1, CIT-1 or CIT-5 structure in the process of  
20 the present invention is also conceivable. Further titanium-containing zeolites which may be mentioned are those having the ZSM-48 or ZSM-12 structure.

As particularly preferred catalysts, specific mention may be made of the titanium-containing zeolite catalysts generally referred to as "TS-1", "TS-2", "TS-3",  
25 "ZSM-48" and "ZSM-12", in each case with Ti, TTM-1, Ti-RUT, titanium-containing zeolites of the types "UTD-1", "CIT-5" and "SSZ-24", and also Ti zeolites having a structure isomorphous with  $\beta$ -zeolite.

For example, use is made of titanium zeolites as are known, for example from  
30 US 3 329 481. In such titanium zeolites, part of the Si(IV) originally present in the silicate lattice is replaced by titanium as Ti(IV). Further titanium zeolites, in particular ones having a crystal structure of the MFI type, and possible ways of preparing them are described, inter alia, in US 4 410 501, EP-A 0 311 983, US 4 666 692, DE-A 3 047 798 or BE 1 001 038, whose relevant contents are  
35 wholly incorporated by reference into the present application. Further titanium-containing zeolites which can readily be used for the purposes of the present invention and have a structure different from the MFI structure are described, for

example, in EP-A 0 405 978. Apart from silicon and titanium, such zeolites may further comprise additional elements such as aluminum (described, for example, in DE-A 31 41 283), gallium (EP-A 0 266 825), boron (US 4 666 692) or small amounts of fluorine (EP-A 0 292 363). The content of the above-described publications relating to the zeolites described there is also wholly incorporated by  
5 reference into the present application.

Further zeolite catalysts which can be used in the process of the present invention are described, for example, in US-A 5,430,000 and WO 94/29408, whose relevant  
10 contents are incorporated by reference into the present application.

Further titanium-containing zeolites which may be mentioned are those having a structure of the ZSM-48 type, the ZSM-12 type, ferrierite or  $\square$ -zeolite and of mordenite.  
15

In addition, the following zeolite catalysts can be used in the process of the present invention:

Catalysts having a zeolite structure as are described in DE-A 196 23 611.8, whose contents relating to the catalysts described therein are hereby wholly incorporated  
20 by reference into the present application.

These are oxidation catalysts based on titanium silicates or vanadium silicates having a zeolite structure; as regards the zeolite structure, reference may be made  
25 to the structures indicated above as preferred. These catalysts are shaped by means of consolidating shaping processes as described in detail in the abovementioned application.

In addition, the process of the present invention can be carried out using catalysts comprising at least one element selected from among the elements of groups Ia, IIa, IIIa, IVa, Va, VIa, VIIa, VIIIa, Ib, IIb, IIIb, IVb, Vb, VIb, VIIb of the Periodic Table.  
30

It is also possible to use oxidation catalysts based on titanium silicates or vanadium silicates having a zeolite structure and a content of from 0.01 to 30% by weight of  
35 one or more noble metals selected from the group consisting of ruthenium, rhodium, palladium, osmium, iridium, platinum, rhenium, gold and silver, which

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have likewise been shaped by consolidating shaping processes. Such catalysts are described in DE-A 196 23 609.6, whose contents relating to the catalysts described there are wholly incorporated by reference into the present application.

- 5 As regards the consolidating shaping processes, the binders and the auxiliaries and the structure of the oxidation catalysts, the relevant contents of DE-A 196 23 611.8 are hereby incorporated by reference.

- 10 The oxidation catalyst described in DE-A 196 23 609.6 has a content of from 0.01 to 30% by weight, in particular from 0.05 to 15% by weight, especially from 0.1 to 8% by weight, in each case based on the amount of the titanium or vanadium zeolites, of the abovementioned noble metals. Particular preference is given to palladium. The noble metals can be applied to the catalyst in the form of suitable noble metal components, for example in the form of water-soluble salts, before,  
15 during or subsequent to the consolidating shaping step.

Furthermore, the following catalysts can be used according to the present invention:

- 20 A shaped body which comprises at least one porous oxidic material and is obtainable by a process comprising the following steps:

- (I) admixing a mixture comprising a porous oxidic material or a mixture of two or more thereof with a mixture comprising at least an alcohol and  
25 water, and
- (II) kneading, shaping, drying and calcining the mixture obtained as described in step (I).

- 30 Details of this catalyst may be found in DE-A 197 23 751.7, whose contents are wholly incorporated by reference into the present application.

- Furthermore, it is also possible, according to the present invention, to use solids which comprise silicon dioxide and are able to be prepared by a process  
35 comprising step (I) below:

- (I) bringing at least one precursor of silicon dioxide into contact with at



least one structure former in a liquid medium, wherein the structure former is a polyethylenimine or a mixture of two or more thereof.

5 Details regarding this solid may be found in DE-A 197 32 865.2, the contents of which are hereby wholly incorporated into the present application.

10 Further catalysts which can readily be used are shaped bodies which comprise an inert support and at least one silicate, preferably a crystalline silicate, applied thereto and are obtainable by application of a mixture comprising at least one silicate and at least one metallic acid ester or a hydrolysate thereof or a combination of metallic acid ester and hydrolysate thereof to the inert support, as described in DE-A 197 54 924.1, whose contents are wholly incorporated by reference into the present application.

15 Furthermore, it is possible, according to the present invention, to use shaped bodies which comprise at least one silicate and at least one metal oxide and are able to be prepared by a process comprising step (i) below:

20 (i) mixing the silicate or silicates with at least one metal oxide solution which has a low content of alkali metal ions and alkaline earth metal ions,

as is described in DE-A 198 15 879.3.

25 The relevant contents of that application are likewise wholly incorporated by reference into the present application.

30 It is also possible, according to the present invention, to use titanium silicalites which have an RUT structure and can be prepared by a process comprising the steps (i) and (ii):

(i) preparation of a mixture of at least one  $\text{SiO}_2$  source and at least one titanium source;

35 (ii) crystallization of the mixture from (i) in a pressure vessel with addition of at least one template compound to give a suspension, wherein the template compound used is an amine or ammonium salt which is

suitable for stabilizing cages of the silicate structure  $[4^45^46^2]$  and  $[4^45^66^58^1]$ .

Details of these catalysts may be found in DE-A 198 39 792.5.

5

It is also possible, according to the present invention, to use the silicon dioxides having mesopores and micropores described in DE-A 198 47 630.2, which preferably have one or more of the features (i) to (iii):

- 10 (i) the sum of the specific surface areas of the mesopores and micropores is at least  $300 \text{ m}^2/\text{g}$ ;
- (ii) the sum of the pore volumes of the mesopores and micropores is at least  $0.2 \text{ ml/g}$ ;
- 15 (iii) the maximum of the pore diameter distribution of the mesopores is at not less than  $3 \text{ nm}$ .

Further details regarding these catalysts may be found in the abovementioned application, whose contents are wholly incorporated by reference into the present application.

20

Sheet silicates are silicates having a two-dimensionally linked silicate lattice and are described, for example, in R.M. Barrer "Zeolites and Clay Minerals as Sorbents and Molecular Sieves", Academic Press 1978, pages 407 ff, in particular pages 413, 421 and 430. Particular mention may be made of attapulgite and sepiolite, pyrophyllite, talc, muscovite, paragonite, phlogopite, biotite, lepidolite, zinnwaldit, margarite, chloritoide, seyberite, vermiculites, smectites, e.g. montmorillonite, saponite, nontronite, beidellite, sauconite, hectorite, fluorhectorite, seladonite, glauconite, dioctahedral illite, trioctahedral illite, beidellite I and beidellite II.

25

30

On the other hand, clathrasils are three-dimensionally linked silicate structures whose network is nevertheless generally so narrow that no molecules having a kinetic diameter above  $0.4 \text{ nm}$  can be taken up, as is described, for example, in B. Marler, H. Gies "Zeolites", 15th edition, pages 5/7 (1995).

35

In a further preferred embodiment of the present process, the above-described

silicate-containing catalysts are regenerated after complete or partial loss of activity and are preferably reused in the reaction according to the present invention. For the regeneration of the catalyst used according to the present invention, it is in principle possible to use all processes known from the prior art  
5 for regenerating silicate-containing catalysts, in particular zeolite catalysts. In general, the used catalyst is treated at from 20 to 700°C in the presence or absence of oxygen or oxygen-donating substances so that the activity of the regenerated catalyst is higher than that of the used catalyst.

10 Specific mention may be made of the methods which have hitherto been described only for zeolite catalysts:

1. a process for regenerating an exhausted (zeolite) catalyst which comprises heating the exhausted catalyst at a temperature below 400°C but above  
15 150°C in the presence of molecular oxygen for a period which is sufficient for increasing the activity of the exhausted catalyst, as is described in EP-A 0 743 094;
2. a process for regenerating an exhausted (zeolite) catalyst which comprises heating the exhausted catalyst at from 150°C to 700°C in the presence of a  
20 gas stream containing not more than 5% by volume of molecular oxygen for a period which is sufficient to improve the activity of the exhausted catalyst, as is described in EP-A 0 790 075;
- 25 3. a process for regenerating (zeolite) catalysts, in which the exhausted catalyst is heated at from 400 to 500°C in the presence of an oxygen-containing gas or is washed with a solvent, preferably at a temperature which is 5-150°C higher than the temperature used during the reaction, as is described in JP 3 11 45 36;
- 30 4. a process for regenerating an exhausted (zeolite) catalyst by calcining it at 550°C in air or by washing with solvents, thus restoring the activity of the catalyst, as is described in "Proc. 7th Intern. Zeolite Conf. 1986 (Tokyo)";
- 35 5. a process for regenerating a (zeolite) catalyst comprising steps (I) and (II) below:

- (I) heating an at least partially deactivated catalyst to a temperature in the range from 250°C to 600°C in an atmosphere containing less than 2% by volume of oxygen, and
- 5 (II) treating the catalyst at a temperature in the range from 250 to 800°C, preferably from 350 to 600°C, with a gas stream having a content of an oxygen-donating substance or of oxygen or of a mixture of two or more thereof in the range from 0.1 to 4% by volume,
- 10 and optionally the further steps (III) and (IV),
- (III) treating the catalyst at a temperature in the range from 250 to 800°C, preferably from 350 to 600°C, with a gas stream having a content of an oxygen-donating substance or of oxygen or of a mixture of two or more thereof in the range from > 4 to 100% by volume,
- 15 (IV) cooling the regenerated catalyst obtained in step (III) in an inert gas stream containing up to 20% by volume of the vapor of a liquid selected from the group consisting of water, alcohols, aldehydes, ketones, ethers, acids, esters, nitriles, hydrocarbons and mixtures of two or more thereof.
- 20
- 25 Details of this process may be found in DE-A 197 23 949.8.

As regards the reaction conditions in the process of the present invention, there are no particular restrictions. The reaction can be carried out at subatmospheric, atmospheric or superatmospheric pressures, depending on the reaction temperature used. This is generally in the range from about 25 to about 150°C, preferably from about 50 to about 120°C and in particular from about 70 to about 100°C.

30

As solvent, it is possible to use either organic solvents or water or mixtures thereof. Preference is given to carrying out the reaction in aqueous solution or suspension.

35

The reaction time is in the range from one minute to a plurality of hours. There are no restrictions in respect of the molar ratio of oxidant to PMIDE; preference is

given to using at least 0.5 mol, more preferably at least 1 mol, of oxidant per mol of PMIDE.

As already mentioned, the reaction mixture can be brought into contact with the catalyst either in suspension or in a fixed bed. The reaction can be carried out batchwise or continuously.

To avoid safety risks, the oxygen content during the reaction is generally set so that the composition is reliably outside the explosive limits. This is achieved, for example, by mixing in suitable inert gases such as nitrogen.

The present invention is illustrated by the examples below:

### Examples:

#### Example 1

In a 250 ml three-necked flask fitted with stirrer, dropping funnel and reflux condenser, 20 g of catalyst (Cr/zeolite having a BEA structure and a chromium content of 2.8% by weight) in 100 ml of deionized water were combined with 34 g of PMIDE and heated to 85°C while stirring. After this temperature had been reached, 70 ml of a 30% strength by weight H<sub>2</sub>O<sub>2</sub> solution were added and the solution was allowed to react for 1 hour. After cooling, the catalyst was separated off and the clear reaction solution was analyzed. The glyphosate content was determined as 3.2% by weight by means of HPLC using UV detection; this corresponds to a yield of 18 mol% based on PMIDE used.

#### Example 2

Example 1 was repeated using 20 g of montmorillonite (bulk density: 670 g/l; specific surface area: 230 m<sup>2</sup>/g) as catalyst. The glyphosate content of the resulting reaction mixture was 6.6% by weight, corresponding to a yield of 44% based on PMIDE used.

We claim:

1. A process for preparing N-phosphonomethylglycine or a salt thereof by bringing phosphonomethyliminodiacetic acid or a salt thereof into contact with at least one oxygen-containing oxidant in the presence of a heterogeneous catalyst comprising at least one silicate.
2. A process as claimed in claim 1, wherein the oxygen-containing oxidant or oxidants is/are selected from the group consisting of hydroperoxides, gases containing molecular oxygen, oxygen-donating compounds, nitrogen oxides and mixtures of two or more thereof.
3. A process as claimed in claim 1 or 2, wherein the silicate or silicates is/are selected from the group consisting of zeolites, sheet silicates, naturally occurring or synthetically produced clay minerals, clathrasils and mixtures of two or more thereof.
4. A process as claimed in claim 3, wherein the crystalline silicate or silicates is/are selected from the group consisting of zeolites of the structure types ABW, ACO, AEI, AEL, AEN, AET, AFG, AFI, AFN, AFO, AFR, AFS, AFT, AFX, AFY, AHT, ANA, APC, APD, AST, ATN, ATO, ATS, ATT, ATV, AWO, AWW, BEA, BIK, BOG, BPH, BRE, CAN, CAS, CFI, CGF, CGS, CHA, CHI, CLO, CON, CZP, DAC, DDR, DFO, DFT, DOH, DON, EAB, EDI, EMT, EPI, ERI, ESV, EUO, FAU, FER, GIS, GME, GOO, HEU, IFR, ISV, ITE, JBW, KFI, LAU, LEV, LIO, LOS, LOV, LTA, LTL, LTN, MAZ, MCM-22, MEI, MEL, MEP, MER, MFI, MFS, MON, MOR, MSO, MTF, MTN, MTT, MTW, MWW, NAT, NES, NON, OFF, OSI, PAR, PAU, PHI, RHO, RON, RSN, RTE, RTH, RUT, SAO, SAT, SBE, SBS, SBT, SFF, SGT, SOD, STF, STI, STT, TER, THO, TON, TSC, VET, VFI, VNI, VSV, WEI, WEN, YUG, ZON and ITQ-4 and mixtures of two or more thereof.
5. A process as claimed in any of claims 1 to 4, wherein the heterogeneous catalyst further comprises at least one element selected from among the elements of groups Ia, IIa, IIIa, IVa, Va, VIa, VIIa, VIIIa, Ib, IIb, IIIb, IVb, Vb, VIb, VIIb of the Periodic Table.

6. A process as claimed in any of claims 1 to 5, wherein the heterogeneous catalyst is regenerated after complete or partial loss of activity and the regenerated heterogeneous catalyst is reused for preparing N-phosphonomethylglycine or a salt thereof from phosphonomethyliminodiacetic acid or a salt thereof.
- 5

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# Declaration, Power of Attorney

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We (I), the undersigned inventor(s), hereby declare(s) that:

My residence, post office address and citizenship are as stated below next to my name,

We (I) believe that we are (I am) the original, first, and joint (sole) inventor(s) of the subject matter which is claimed and for which a patent is sought on the invention entitled

Preparation of glyphosate or a salt thereof

the specification of which

☒ is attached hereto.

☐ was filed on \_\_\_\_\_ as

Application Serial No. \_\_\_\_\_

and amended on \_\_\_\_\_.

☒ was filed as PCT international application

Number PCT/EP00/07003

on 21/07/2000

and was amended under PCT Article 19

on \_\_\_\_\_ (if applicable).

We (I) hereby state that we (I) have reviewed and understand the contents of the above-identified specification, including the claims, as amended by any amendment referred to above.

We (I) acknowledge the duty to disclose information known to be material to the patentability of this application as defined in Section 1.56 of Title 37 Code of Federal Regulations.

We (I) hereby claim foreign priority benefits under 35 U.S.C. § 119(a)–(d) or § 365(b) of any foreign application(s) for patent or inventor's certificate, or § 365(a) of any PCT International application which designated at least one country other than the United States, listed below and have also identified below, by checking the box, any foreign application for patent or inventor's certificate, or PCT International application having a filing date before that of the application on which priority is claimed. Prior Foreign Application(s)

Application No.	Country	Day/Month/Year	Priority Claimed
19934599.6	Germany	23 July 1999	<input checked="" type="checkbox"/> Yes <input type="checkbox"/> No



We (I) hereby claim the benefit under Title 35, United States Codes, § 119(e) of any United States provisional application(s) listed below.

\_\_\_\_\_  
(Application Number)

\_\_\_\_\_  
(Filing Date)

\_\_\_\_\_  
(Application Number)

\_\_\_\_\_  
(Filing Date)

We (I) hereby claim the benefit under 35 U.S.C. § 120 of any United States application(s), or § 365(c) of any PCT International application designating the United States, listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States or PCT International application in the manner provided by the first paragraph of 35 U.S.C. § 112, I acknowledge the duty to disclose information which is material to patentability as defined in 37 CFR § 1.56 which became available between the filing date of the prior application and the national or PCT International filing date of this application.

Application Serial No.

Filing Date

Status (pending, patented,  
abandoned)

_____	_____	_____
_____	_____	_____
_____	_____	_____
_____	_____	_____

2 And we (I) hereby appoint Messrs. **HERBERT B. KEIL**, Registration Number 18,967; and **RUSSEL E. WEINKAUF**, Registration Number 18,495; the address of both being Messrs. Keil & Weinkauff, 1101 Connecticut Ave., N.W., Washington, D.C. 20036 (telephone 202-659-0100), our attorneys, with full power of substitution and revocation, to prosecute this application, to make alterations and amendments therein, to sign the drawings, to receive the patent, and to transact all business in the Patent Office connected therewith.

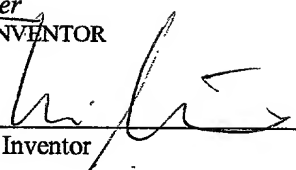
We (I) declare that all statements made herein of our (my) own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

**Declaration**

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